

between the experimental and calculated resistivities, when using the valence given by the measured Hall coefficient, suggests that the number of conduction electrons in the alloy may indeed be larger than expected from the normal valences. The volume dependence of the Hall coefficient at constant temperature of pure mercury would greatly assist the solution to this question.

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## ANOMALOUS PHONON EFFECTS ON SPECIFIC HEAT AND SPIN-LATTICE RELAXATION IN CERIUM ETHYL SULFATE\*

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The hitherto unexplained extra specific heat and fast spin-lattice relaxation in cerium ethyl sulfate are explained by an anomalous phonon spectrum calculated using thermodynamic Green's functions for incoherent spins and phonons.

For the  $\text{Ce}^{3+}$  ion in cerium ethyl sulfate (CES), the lowest crystal-field states are the three  $J = \frac{5}{2}$  Kramers doublets. The first excited doublet is at  $E_0 = 6.8^\circ\text{K}$  above the ground doublet and the second excited doublet is at  $E_1 \approx 150^\circ\text{K}$ .<sup>1,2</sup> Near the peak of the Schottky specific heat associated with the two lowest  $\text{Ce}^{3+}$  doublets, there is a hitherto unexplained contribution. After subtracting the normal lattice specific heat, the entropy calculated<sup>3,4</sup> (from what should be the residual  $\text{Ce}^{3+}$  specific heat associated with the two lowest doublets) is greater than  $R \ln 4$  for  $T > 12^\circ\text{K}$ . This cannot be accounted for by the population of the doublet at  $E_1 = 150^\circ\text{K}$ .

To explain the extra specific heat and entropy, perturbation and Green's function calculations based on strong spin-phonon interaction have been attempted by a number of authors.<sup>5,6</sup> In all these calculations the two doublets are treated as an effective spin- $\frac{1}{2}$  state whose levels are split by an energy  $E_0$ . Rather than the general spin-phonon interaction, a linearized interaction is used. The Hamiltonian then has the form

$$\mathcal{H} = -E_0 \sum_{i=1} S_{iz} + \sum_{\vec{k}, p} E_{\vec{k}p} (a_{\vec{k}p}^\dagger a_{\vec{k}p} + \frac{1}{2}) + \frac{1}{\sqrt{N}} \sum_{L=1}^N \sum_{\vec{k}, p} A_{\vec{k}p} \exp(i\vec{k} \cdot \vec{r}_i) (a_{\vec{k}p}^\dagger + a_{-\vec{k}p}) (S_{i+} + S_{i-}), \quad (1)$$

where  $S_{iz}$  and  $S_{i\pm}$  are spin operators at lattice site  $i$ ,  $N$  is the number of spins,  $N_L$  is the number of unit cells,  $a_{\vec{k}p}^\dagger$  and  $a_{-\vec{k}p}$  are phonon creation and annihilation operators,  $E_{\vec{k}p}$  is the energy of a phonon with wave vector  $\vec{k}$  and polarization  $p$ , and  $A_{\vec{k}p}$  is the spin-phonon coupling energy. Because of the phase factor  $\exp(i\vec{k} \cdot \vec{r}_i)$  in the Hamiltonian, the elementary excitations at different lattice sites are

not independent of each other. Rather they have the form of coupled spin waves and phonons with the same wave vector  $\vec{k}$ . Using the Hamiltonian (1) even the most recent calculation with an improved decoupling scheme for the Green's functions does not predict the form of the observed specific heat anomaly and also rigorously yields no extra entropy.<sup>6</sup>

For this problem, a key fact is that no spin-spin or spin-phonon interaction can change the spin contribution to the total entropy, which is always  $R \ln n_s$  (where  $n_s$  is the number of spin states per ion). Therefore, after subtracting the normal lattice contribution the observed extra entropy for CES above  $R \ln 4$  for  $T > 12^\circ\text{K}$  must come from a change of the phonon properties arising from the presence of the spin-phonon interaction.

To explain the specific-heat anomaly, we performed a new Green's function calculation in which we accounted for a previously neglected experimental observation. Thermal-conductivity<sup>7</sup> and infrared absorption<sup>8</sup> measurements show that the direct phonon and photon transitions between the lowest two  $\text{Ce}^{3+}$  doublets have extremely broad resonance linewidths of  $(3 \pm 1)^\circ\text{K}$ , which is much larger than the linewidth due to the excited doublet lifetime. Since the average splitting  $E_0$  between the two doublets is only about  $6.8^\circ\text{K}$ , the effect of this broadening must be included in the Hamiltonian. This was not done in previous calculations. The broad linewidth implies that the splittings of the lowest two doublets for an ensemble of  $\text{Ce}^{3+}$  ions are widely distributed around a mean energy  $E_0$ . Therefore, ions with the same splitting energy  $E'$  are widely separated in space and a given phonon with a given energy near  $E_0$  can interact only with a relatively small number of  $\text{Ce}^{3+}$  ions. Since these phonons undergo scattering on imperfections in the relatively soft CES lattice, this has the consequence of averaging out the phonon-phase factor  $\exp(i\vec{k} \cdot \vec{r}_i)$  in the Hamiltonian (1) to give a new Hamiltonian:

$$\mathcal{K}' = - \int_{-\infty}^{\infty} N_L^{-1/2} S_{0z} E' c \xi(E') dE' + \sum_{\vec{k}, p} E_{\vec{k}p} (a_{\vec{k}p}^\dagger a_{\vec{k}p} + \frac{1}{2}) + \int_{-\infty}^{\infty} \sum_{\vec{k}, p} A_{\vec{k}p}(E') (a_{\vec{k}p}^\dagger + a_{-\vec{k}p}) (S_{0+} + S_{0-}) c \xi(E') dE', \quad (2)$$

where  $\xi(E')$  is the normalized distribution function of the splitting energies,  $c = N/N_L$  is the spin concentration per unit cell, and

$$S_{0\nu} = N_L^{-1/2} \sum_{i=1}^{N_L} S_{i\nu}$$

are the spin-wave operators for  $\vec{k} = 0$ , where  $\nu = z, +, \text{ and } -$ .

With (2) as the Hamiltonian, the problem is reduced to the interaction of phonons with single spins of concentration  $c$ . The excitation modes corresponding to this Hamiltonian are qualitatively different from those of (1) because no spin excitations with  $\vec{k} > 0$  are possible. To get the thermodynamic properties of the system described by (2), we calculate from the double-time Green's functions<sup>9</sup>  $\langle S_{0+} S_{0-} \rangle$ ,  $\langle a_{\vec{k}}^\dagger a_{\vec{k}} \rangle$ ,  $\langle S_{0\pm} a_{\vec{k}} \rangle$ ,  $\langle S_{0\pm} a_{\vec{k}}^\dagger \rangle$  with the help of a rigorous consistency condition which relates phonon and spin-phonon Green's functions to the spin Green's functions. To account for deviations in the phonon spectrum, Green's functions were calculated up to second order and decoupled as follows:

$$\langle\langle a_{-\vec{k}}^\dagger a_{\vec{k}}^\dagger, S_{0\pm} | S_{0-} \rangle\rangle - \langle a_{-\vec{k}}^\dagger a_{\vec{k}}^\dagger \rangle \langle\langle S_{0\pm} | S_{0-} \rangle\rangle; \langle\langle S_{iz} S_{j\pm} | S_{0-} \rangle\rangle - \langle S_{i-} \rangle \langle\langle S_{j\pm} | S_{0-} \rangle\rangle, \quad i \neq j.$$

To carry the calculations to completion,<sup>10</sup> we make some further physical assumptions: (1) The spin-phonon scattering is more important than any other phonon scattering mechanism, as indicated by the thermal conductivity measurements on CES.<sup>7</sup> (2) The broad transition linewidth between the two doublets is much greater than the contribution to the lifetime linewidth associated with spin-phonon relaxation, which in turn is much greater than the contribution to the lifetime linewidth associated with spin-spin relaxation (as indicated by the relaxation experiments mentioned later in this paper). (3) The average splitting  $E_0$  is much less than the Debye energy  $E_D$  ( $60^\circ\text{K}$  for CES). (4) The only phonons interacting with the  $\text{Ce}^{3+}$  ions are the longitudinal acoustic phonons for which we will assume the well-known Debye approximation. (5) We choose a Gaussian transition lineshape for  $\xi(E')$  centered on  $E_0$  with a half-half width of  $\delta$ .

In second order we find the same result for  $\langle S_{iz} \rangle$  as in a system without spin-phonon interaction:

$$\langle S_{iz} \rangle = f(E') = \frac{1}{2} \tanh(E'/2T)$$

for the ions whose lowest two doublets have the splitting  $E'$ . The second-order phonon Green's functions relate  $\langle a_{\vec{k}}^\dagger a_{\vec{k}} \rangle$  to  $\langle S_{iz} \rangle$  and for a longitudinal acoustic mode with energy  $E_{\vec{k}}$  we find an anomalous occupation number:

$$\langle a_{\vec{k}}^\dagger a_{\vec{k}} \rangle \equiv [\exp(E_{\vec{k}}/T) - 1]^{-1} + cf(E_{\vec{k}}) \left( \frac{2}{\pi} \right)^{1/2} \frac{E_{\vec{k}}}{6\delta} \left( \frac{E_D}{E_0} \right)^3 \tanh\left( \frac{E_{\vec{k}}}{2T} \right) [\exp(E_{\vec{k}}/T) - 1]^{-1} \exp \left[ -\frac{1}{2} \left( \frac{E_{\vec{k}} - E_0}{\delta} \right)^2 \right]$$

in the limiting case when the spin-phonon relaxation rate  $\Gamma_{sl}$  is much larger than the spin-spin relaxation rate  $\Gamma_{ss}$ . [In the opposite case when spin-phonon relaxation becomes slower than spin-spin relaxation, the second term in  $n_{\vec{k}}$  disappears with the dependence  $r_{sl}/(r_{sl} + r_{ss})$ .] The first term in  $n_{\vec{k}}$  is the normal Bose-Einstein occupation number and the second term, which we call  $\Delta n_{\vec{k}}$ , implies that there are extra phonons excited in a given phonon mode at thermal equilibrium.

Assuming an isotropic Debye spectrum for the phonon density of states, we find for the energy of the longitudinal acoustic phonons

$$E_p(T) = \sum_{\vec{k}} E_{\vec{k}} n_{\vec{k}} = (3N_L/E_D^3) \int_0^{E_D} E_k^3 n_k dE_k$$

from which the lattice specific heat is  $dE_p/dT$ . If we take  $\delta \ll E_0$ , we find an extra lattice specific heat from  $\Delta n_{\vec{k}}$  which is

$$\frac{\Delta C_L}{R} = \frac{1}{2} c \left[ \tanh\left( \frac{E_0}{2T} \right) - \frac{1}{2} \right] \left( \frac{E_0}{T} \right)^2 \frac{e^{E_0/T}}{(1 + e^{E_0/T})^2}$$

At low  $T$  this is almost proportional to the Schottky specific heat. Note the linear dependence on  $c$  in both  $\Delta n_{\vec{k}}$  and  $\Delta C_L/R$ . This reflects the fact that there exist only single-spin excitations in our model. For CES with  $c=2$  (since there are two  $Ce^{3+}$  ions per unit cell), the extra specific heat is large and is a fair approximation to the experimental extra specific heat, as shown in Fig. 1(b).

For CES we know the transition linewidth is perhaps as large as 4°K, and we have done a computer calculation to account for this both in  $\Delta C_L/R$  and in the Schottky spin specific heat. There occurs a slight broadening at high and low

$T$  and about a 5% reduction of the specific heat near the Schottky peak, as shown in Fig. 1(c).

Besides producing an extra specific heat, the extra phonons represented by  $\Delta n_{\vec{k}}$  imply a serious effect on the direct spin-lattice relaxation between the lowest two doublets of  $Ce^{3+}$  in CES. This relaxation rate and the Orbach relaxation rate within the ground doublet, which depends on the same spin-phonon transitions, are both proportional to  $n_{\vec{k}}$  times the density of states in first order time-dependent perturbation theory.<sup>11</sup> Using the Debye approximation for the density of states and again using a Gaussian transition lineshape with  $\delta \ll E_0$ , the term  $\Delta n_{\vec{k}}$  leads to a multiplicative factor in both relaxation rates of

$$\alpha = \frac{c}{6(2\pi)^{1/2}} \frac{E_0}{\delta} \left( \frac{E_D}{E_0} \right)^3 \tanh^2\left( \frac{E_0}{2T} \right). \quad (3)$$

For CES with  $c=2$ , the value of  $\alpha$  for  $T < 4^\circ K$  is approximately 400 for the linewidth  $2\delta \approx 3^\circ K$ . This factor implies a large increase in the spin-lattice relaxation rates of  $Ce^{3+}$  in CES compared with those of  $Ce^{3+}$  diluted into other isomorphous rare-earth ethyl sulfate hosts (RES) for which  $c \ll 2$ .

For  $Ce^{3+}$  diluted into other rare-earth ethyl sulfates,  $E_0$  and  $E_1$  vary widely as  $R$  is varied. In several RES Larson<sup>12</sup> found a dominant Orbach spin-lattice relaxation rate<sup>11</sup> for the ground doublet of  $Ce^{3+}$  which follows in an extremely systematic way the theoretical Orbach rate:

$$1/\tau = A E_0^3 [e^{E_0/T} - 1]^{-1}$$

with  $A$  approximately constant for all RES. Assuming the normal phonon spectrum, we would expect the same value of  $A$  for  $Ce^{3+}$  in CES so that, with  $E_0 = 6.8^\circ K$ , the relaxation rate for  $Ce^{3+}$  in CES should be

$$1/\tau = 4 \times 10^6 [e^{6.8/T} - 1] \text{ sec}^{-1}$$

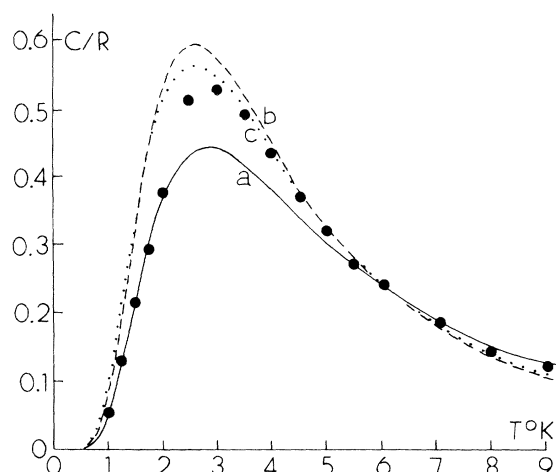


FIG. 1. Specific heat of cerium ethyl sulfate. Closed circles: measured specific heat minus the normal lattice specific heat (Ref. 3). (a) The Schottky specific heat for  $E_0 = 6.8^\circ\text{K}$ . (b, c) The Schottky plus the extra lattice specific heat for (b)  $\delta < 6.8^\circ\text{K}$ , (c)  $\delta = 2^\circ\text{K}$ .

Larson attempted to measure this rate in CES but found no response.<sup>13</sup> This indicated that the relaxation rate is much faster than the above estimate.

We have found a fast relaxation rate in CES using the high-frequency relaxation method<sup>14</sup> to measure the real part of the magnetic susceptibility  $\chi'$  at frequencies  $\omega > 10$  MHz,  $T < 4.2^\circ\text{K}$ , and  $0 \leq H \leq 15$  kG. Experimentally,  $\chi'$  approximately obeys a Debye relation. The relaxation rate calculated from  $\chi'$  in zero magnetic field is

$$1/\tau = (8 \pm 1) \times 10^9 [e^{6.8/T} - 1]^{-1} \text{ sec}^{-1}$$

and the rate decreases to a high-field limit (for  $H \geq 4$  kG) of

$$1/\tau = (3.5 \pm 0.5) \times 10^9 [e^{6.8/T} - 1]^{-1} \text{ sec}^{-1}.$$

Our analysis of the susceptibility measurements<sup>15</sup> leads us to conclude that this relaxation is indeed the Orbach spin-lattice relaxation within the ground doublet caused by the direct spin-phonon transitions between the lowest two doublets. We also conclude from our analysis that all spin-spin relaxation mechanisms are much less important than this spin-lattice process.<sup>16</sup>

We see that the magnitude of this Orbach rate in CES is over 1000 times larger than the rate predicted from Larson's measurements on  $\text{Ce}^{3+}$  diluted into RES. However, this is straightforwardly explained from the anomalous phonon spectrum which we have calculated for CES. The

experimental enhancement factor of 1000 is quite close to the value of  $\alpha$  of 400 calculated from Eq. (3).

Other systems with low-lying crystal-field states obviously may show anomalous effects similar to those we have described for CES. In fact praseodymium ethyl sulfate has the same type of specific-heat anomaly and entropy increase near the peak of the  $\text{Pr}^{3+}$  Schottky specific heat.<sup>3</sup> Another possible system is a Kramers doublet split by a large magnetic field. This closely corresponds to the effective spin- $\frac{1}{2}$  representation used in our Green's-function calculation. If the field is large enough, the spin-spin relaxation between the two states might be made small compared with direct spin-phonon relaxation.

To see a specific-heat alteration and a relaxation-rate enhancement in systems other than CES, we emphasize finally some specific required conditions. First,  $E_0 \ll E_D$ . Second, the transition linewidth must be broad. Third, spin-spin relaxation between the states separated by  $E_0$  must be less important than spin-phonon relaxation.

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<sup>16</sup>One such spin-spin interaction for CES is the electric quadrupole-quadrupole interaction (EQQ) between a  $\text{Ce}^{3+}$  ion  $i$  in the ground doublet and a neighboring  $\text{Ce}^{3+}$  ion  $j$  in the first excited doublet [B. Bleaney, *Proc. Phys. Soc. (London)* **77**, 113 (1961); J. M. Baker,

*Phys. Rev.* **136**, A1633 (1964)]. This cannot cause the observed large increase in the relaxation rate between the two  $\text{Ce}^{3+}$  doublets because the EQQ operator  $O_2^m(i)O_2^{-m}(j)$  gives only an energy-conserving cross-relaxation process. Also, the rapid disappearance of  $\chi'$  for  $H=0$  and high  $\omega$  and low  $T$  shows that magnetic dipole interactions are unimportant for relaxation within the  $\text{Ce}^{3+}$  ground doublet compared with the observed Orbach spin-lattice relaxation process.

### PHOTOINDUCED REVERSIBLE CHARGE-TRANSFER PROCESSES IN TRANSITION-METAL-DOPED SINGLE-CRYSTAL $\text{SrTiO}_3$ AND $\text{TiO}_2$ †

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When  $\text{SrTiO}_3$  or  $\text{TiO}_2$  doped with certain transition elements is irradiated with light in the region 0.39 to 0.43  $\mu$ , broad visible absorption bands with peak absorption as high as 100  $\text{cm}^{-1}$  are introduced. The study of optical and EPR spectra of Fe/Mo doped crystals under the influence of light and various heat treatments shows that the effect is due to a transfer of charge between Fe and Mo ions such that the nonabsorbing  $\text{Fe}^{3+}$  and  $\text{Mo}^{6+}$  ions become  $\text{Fe}^{4+}$  and  $\text{Mo}^{5+}$  with absorption bands in the visible.

We have observed large reversible changes in the optical absorption of certain transition-metal-doped  $\text{SrTiO}_3$  and  $\text{TiO}_2$  single crystals after irradiation with visible light in the region 0.39–0.43  $\mu$ . The effect can be explained as a photoinduced transfer of charge between the transition metal ion and another defect center present in the crystal. When Mo co-doping is used, the transfer of charge takes place between two known impurities and the size of the effect can be made quite large by increasing the concentration of both dopants.

Such photoinduced charge-transfer processes have been reported before in other inorganic crystals. For example, defect centers in alkali halides and certain glasses have been found to be photochromic.<sup>1,2</sup> Reversible color changes in  $\text{TiO}_2$ ,  $\text{SrTiO}_3$ , and other oxide powders have also been reported.<sup>3</sup> However, these early experiments depended on surface effects, according to some authors.<sup>3</sup> Only qualitative results from visual observation were reported, although the models proposed to explain these effects have some similarity to ours. Charge-transfer processes in phosphors have been studied recently, especially by EPR techniques.<sup>4</sup> In most cases the change in absorption coefficient is not large and the quantum efficiency of coloration is often quite small. We have observed peak absorption-coefficient changes in the visible greater than

100  $\text{cm}^{-1}$  for samples of 0.5-mm thickness or less and quantum efficiencies of approximately 10%. The combined study of the optical and EPR spectra of these materials under the influence of bleaching and coloring light and after various heat treatments permits an identification of the valence states of the various ions responsible for the optical absorption.

Figure 1 shows the optical absorption spectra for Fe/Mo-doped  $\text{SrTiO}_3$  and  $\text{TiO}_2$  at 77°K. Pure  $\text{SrTiO}_3$  and  $\text{TiO}_2$  are transparent in the visible. When either crystal is doped with Fe, a small amount of visible absorption is introduced. This appears as a smearing out of the band edge absorption to longer wavelengths, as shown in Fig. 1. When the sample is irradiated with light in the vicinity of 0.40  $\mu$ , several broad absorption bands are introduced, covering the entire visible region. The individual absorption bands are not well distinguished in a plot such as Fig. 1 because at least one of the absorption peaks usually occurs close to the smeared-out band-edge absorption region. They become more distinct when the difference between the induced and normal optical absorption is plotted. The interpretation and uniqueness of these bands is further demonstrated by the heat-treatment experiments discussed later.

The thermal bleaching rate of the photoinduced state varies widely, depending on both dopant